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TITLE: Treatment of composite polyamide membranes with compatible oxidants

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INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Cadotte; John E.	Minnetonka	MN		
Racchini; Joel R.	St. Louis Park	MN		

ASSIGNEE-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
The FilmTec Corporation	Minneapolis	MN			01

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PRIOR-ART-DISCLOSED:

U.S. PATENT DOCUMENTS

	Search Selected	Search ALL
PAT-NO	ISSUE-DATE	PATENTEE-NAME
<u>4814399</u>	March 1989	Sansone et al.
		US-CL
		528,435

ART-UNIT: 136

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ABSTRACT:

A reverse osmosis membrane having improved rejection of sulfuric acid and/or isopropanol is described. The membrane is prepared by treating a crosslinked, polyamide discriminating layer with a compatible oxidizing reagent, such as peracetic acid, periodic acid or chloramine, whereby the passage through the treated membrane of sulfuric acid in a 2 percent aqueous solution at a transmembrane pressure of 400 psi is reduced by at least 30 percent.

22 Claims, 0 Drawing figures

Exemplary Claim Number: 1,14

BRIEF SUMMARY.

BACKGROUND OF THE INVENTION

This invention relates to treatment of composite polyamide reverse osmosis membranes. More specifically, treatment of polyamide membranes to enhance rejection of certain acids and organic materials in a reverse osmosis process is contemplated.

Removal of materials dissolved or dispersed in a solution by separation of these materials from the dispersing medium or solvent utilizing reverse osmosis membranes is well known. The membranes used for reverse osmosis are selectively permeable to certain components of the mixture to be separated. Generally, water is the component to which such membranes are especially permeable. An aqueous feed solution is conveniently brought in contact with one surface of the reverse osmosis membrane under pressure so as to effect selective permeation of water through the membrane. This process is most generally used for desalination of water-containing salts. However, reverse osmosis has also been used to separate organic compounds and other materials from aqueous feed solutions.

The performance of reverse osmosis membranes has a critical effect on the efficiency and efficacy of reverse osmosis processes. Advantageously, the reverse osmosis membrane should be relatively impermeable to materials which are to be separated from the water and highly permeable to water. It has been found that membranes having a porous support which provides physical strength but imparts little or no rejection, combined with a thin discriminating layer adherent to the support, are particularly useful. Such membranes are commonly referred to as thin film composite membranes.

Polyamide membranes have been widely employed in reverse osmosis processes. U.S. Pat. No. 4,277,344 describes a variety of membranes having a polyamide discriminating layer on a porous support. These membranes are preferably prepared by interfacial polymerization of a difunctional aromatic amine such as meta-phenylene diamine and a trifunctional aromatic acyl halide, such as trimesoyl chloride, optionally containing difunctional acyl halide. A 1,3,5-cyclohexane tricarboxyl chloride can also be employed as the acyl halide reactant. Such membranes are further illustrated in U.S. Pat. Nos. 4,520,044 and 4,606,943. European Patent Application Publication No. 211,633 also describes composite polyamide membranes.

The treatment of membranes to enhance performance is described in the prior art in a number of patents. U.S. Pat. No. 3,551,331 describes a process for modifying the permeability of a substantially linear aliphatic polyamide membrane. In this process, the polyamide membrane is treated with a protenic acid, lyotropic salt or a Lewis acid.

U.S. Pat. No. 3,877,978 describes use of copolymers of vinyl acetate with various ethylenically unsaturated carboxylic acids to enhance the rejection of certain semi-permeable membranes.

U.S. Pat. No. 3,886,066 discloses the use of hydrolyzable tannins to reduce the salt passage through semi-permeable membranes.

U.S. Pat. No. 3,951,315 describes a composite semi-permeable membrane formed of an ultrathin film of polyethylenimine on a support, where said film has been crosslinked with difunctional or trifunctional acylhalides, chlorotannates, isocyanates and sulfonyl chlorides.

U.S. Pat. No. 4,214,020 describes a process for coating exteriors of hollow fiber membranes to enhance their membrane characteristics.

U.S. Pat. No. 4,634,531 describes the use of sequential treatment with a water-soluble amine and a water-soluble aldehyde to improve selective permeation.

U.S. Pat. No. 4,704,324 teaches preparation of membranes by reaction of a nucleophilic first compound with a second compound bearing reactive onium groups.

U.S. Pat. No. 4,812,238 describes the treatment of composite polyamide membranes with nitrous acid or a diazonium compound. The nitrous acid is disclosed to react with pendant amine groups.

U.S. Pat. No. 4,828,700 discloses that reverse osmosis membranes can be treated with polymers bearing carboxylic acid groups and optionally pendant hydroxyl or amide moieties to enhance salt rejection.

U.S. Pat. No. 3,904,519 describes treatment of linear aromatic polyamides with certain crosslinking reagents to improve flux or flux stability of the resulting membranes. Crosslinking reagents employed include aldehydes, polyamines, polycarboxylic acids, polyisocyanates, oxidizing agents, peroxides and other compounds.

Existing commercial composite polyamide membranes display a good combination of high water flux, good salt rejection and acceptable chemical stability. Membranes which are more tolerant of acidic or basic conditions and which demonstrate a higher rejection for organic materials while maintaining high water flux are still sought.

SUMMARY OF THE INVENTION

A method of treating a clean, composite, crosslinked polyamide reverse osmosis membrane to enhance rejection of certain organic compounds and sulfuric acid has now been discovered. This method comprises contacting a composite membrane having a clean, crosslinked polyamide discriminating layer with a solution of an effective amount of a compatible oxidizing reagent, whereby the passage through the membrane of sulfuric acid in a two percent aqueous solution at 400 psig and 25 degree C. is reduced by at least 20 percent, more preferably 50 percent, relative to the membrane prior to treatment and the water flux of said membrane is reduced by not more than 50 percent, preferably not more than 40 percent, after treatment.

In another aspect, the invention is a composite crosslinked polyamide membrane which has been treated by the method described hereinbefore. This membrane possesses novel properties in its combination of high sulfuric acid rejection, high rejection of isopropyl alcohol and certain other organic compounds and excellent water flux. Surprisingly, it has been found that such treated membranes exhibit higher rejection for selected solutes than the untreated membrane with minimum loss of flux in separation of water from aqueous sulfuric acid or aqueous organic streams.

DETAILED DESCRIPTION:

DETAILED DESCRIPTION OF THE INVENTION

Composite reverse osmosis membranes having crosslinked polyamide discriminating layers are well-known. The discriminating layer is advantageously derived from reactants comprising: (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acyl halide groups. The amine and acid halide reactants may be aliphatic, cycloaliphatic or aromatic. Aromatic amines, that is compounds wherein one or more amine groups are bonded to a carbon atom in an aromatic ring, are especially preferred. The amine compound may contain one or two fused or separate aromatic rings in preferred embodiments.

The carboxylic acid halide reactant employed to prepare the polyamide discriminating layer desirably includes an aromatic acyl halide bearing at least three acyl halide groups. The carboxylic acid halide reactant may comprise some compounds or polymers which are difunctional. Preferably, at least 50 mole percent of the carboxylic acid halide reactant is trifunctional or more highly functionalized. The compound bearing the two acyl halide groups optionally bear other substituents which do not interfere with the reaction forming the membrane. Preferably, the carboxylic acid halide is trimesoyl halide. Advantageously, the carboxylic acid halide reactant is trimesoyl halide or cyclohexane-1,3,5-tricarbonyl halide or mixtures of these trifunctional acyl halides. Optionally, isophthaloyl halide and/or terephthaloyl halide may be

employed with one or both of the trifunctional acyl halides. The halide is preferably chloride, but may be bromide.

The aromatic amine compound optionally may bear other substituents which do not interfere with the membrane formation reaction. For example, a compound bearing two primary amine groups and one group which has a carbonyl function not adjacent to the amine group, as described in U.S. Pat. No. 4,761,234, may be employed but is not preferred. The preferred amine reactant employed to form the membrane is prenylene diamine, more preferably meta-phenylene diamine.

The composite crosslinked polyamide membrane can be prepared by techniques known in the prior art. Conveniently, interfacial polymerization of an aqueous amine applied to a microporous substrate with an acyl halide in an organic solution, such as described in U.S. Pat. No. 4,277,344, can be employed and is incorporated herein by reference. Preferred as an organic solvent is an aliphatic hydrocarbon such as hexane, or a chlorofluorocarbon, such as 1,1,2-trichlorotrifluoroethane. Other similar techniques for preparing such membranes are described in U.S. Pat. Nos. 4,606,943; 4,520,044; 4,761,234; 4,772,394; and 4,826,760, and are incorporated herein by reference.

The microporous substrate on which these composite membranes are formed can be any substrate conveniently employed for this purpose. Suitable substrates for composite membranes have been extensively described in the prior art. Illustrative support materials include organic polymeric material such as polysulfone, polyether sulfone, chlorinated polyvinylchloride, styrene/acrylonitrile copolymer, polybutylene terephthalate, cellulose esters and other polymers which can be prepared with a high degree of porosity and controlled pore size distribution. Porous inorganic material may also be operable as supports. Preferably, the surface pores in the support material will have a diameter 2000 ÅNG. or less, and the support material will have as high a porosity as is possible, while maintaining the desired pore size, integrity, and strength. Especially preferred as support layers are porous polysulfone films. These films are generally cast on non woven fabric or woven cloth in the manner described in U.S. Pat. No. 4,277,344. Surface active agents may be employed in the aqueous amine solution to enhance wetting of a hydrophobic substrate.

Especially preferred as membranes to be treated by the method described herein are the membranes disclosed in U.S. Pat. No. 4,277,344. In preferred embodiments, these membranes are prepared by interfacial polymerization of meta-prenylene diamine and trimesoyl chloride. Such membranes are sold by FilmTec Corporation under the designation FT30 membranes.

In one embodiment of the invention, the membrane may be derived from amine reactants or acyl halide reactants which are polymeric. For example, a polymer made by reaction of a difunctional aromatic amine with trimellitic anhydride acid halide optionally mixed with trimesoyl halide, as described in U.S. Pat. No. 4,606,943, is operable as the amine reactant, but is not preferred.

The polyamide of the membrane discriminating layer is crosslinked. These polyamides preferably have a crosslink density of at least about 10 crosslinks, more preferably at least about 50 crosslinks, per 100,000 molecular weight. The crosslink density can be determined by standard end-group analysis techniques and may be estimated by the insolubility or swelling of the resulting polyamide in solvents in which linear polyamides are soluble.

The rejection by the polyamide reverse osmosis membrane of specific solutes and the water flux of the membrane prior to treatment can operably vary over a wide range. The flux and rejection of specific solutes is determined with reference to test conditions using a specific concentration of solute at a specific pressure and temperature. Preferably, the membrane to be treated will have a sodium chloride rejection of at least about 90 percent, more preferably 95 percent, and a water flux of at least about 12 gallons per square foot per day (gfd), more preferably at least about 15 gfd, when tested using an aqueous 0.2 weight percent sodium chloride solution at a transmembrane pressure of 200 lbs./sq. inch (psi) at 25.degree. C. Membranes having a higher salt rejection and useful with seawater feed at a pressure of 800 psi at 25.degree. C. with a flux of 10 gfd may also be treated. Membranes having a much higher flux and lower salt rejection prepared as described in U.S. Pat. No. 4,765,397, which is incorporated by reference, can also be employed.

It is found that the membranes to be treated by the method of this invention are desirably clean. In this context a "clean" membrane is a membrane which has not been subject to extensive service wherein the membrane flux or performance has been reduced by fouling. It has been found that membranes which are freshly prepared and have been subjected to only a brief test, (preferably less than 24 hours, more preferably less than 1 hour) to determine initial reverse osmosis performance or no test prior to treatment are particularly suitable to the treatments of this invention. Membranes which have been in service for an extended time and then are cleaned by standard techniques after being fouled are not as susceptible to treatment by the method of this invention.

The term "compatible oxidizing reagent" as used herein refers to oxidizing agents which do not deleteriously affect the properties of the composite membrane when employed for a short time period. Preferably, the compatible oxidant has a molecular weight less than about 300, more preferably less than about 150. Such compatible oxidizing reagents do not include strong oxidants, such as sodium hypochlorite, the use of which is suggested in U.S. Pat. No. 4,277,344. However, it should be noted that treatment with sodium hypochlorite has been found in some instances to enhance sulfuric acid rejection of composite polyamide membranes.

The reagent preferably contacts the discriminating layer of the composite crosslinked polyamide membrane while in a liquid diluent. Preferably, this diluent does not deleteriously affect either the discriminating layer or the support layer of the composite membrane. Advantageously, the oxidizing reagent is dissolved in the diluent. The suitability of a diluent will depend upon the specific composition of the desalinizing layer, the nature of the oxidizing reagent and the composition of the support. An effective amount of the reagent is employed to impart the desired rejection properties to the membrane after treatment without deleterious effects on the membrane. An aqueous solution of from 0.1 to about 1 percent of the oxidizing reagent is generally preferred. Diluents other than water may be preferred if water will react with the reagent. Co-solvents can be employed with water but are generally not necessary nor desirable. Suitable co-solvents include the lower alkanols, such as isopropanol or ethanol, and amides, such as N,N-dimethylformamide.

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is most preferably monomeric or substantially monomeric and has a molecular weight of less than about 100.

The temperature during treatment of the membrane is desirably maintained so as to avoid deleterious effects on the membrane. Too high a temperature may reduce flux and/or salt rejection by the membrane while too low a temperature may lead to undesirably long contact times for the treatment. Generally, temperatures in the range from about 15 degree. to about 50 degree. C., preferably about 20 degree. to about 35 degree., are advantageous.

The treatment is conveniently conducted at atmospheric pressure, but a positive transmembrane pressure differential can optionally be employed.

The treatment of composite, crosslinked polyamide reverse osmosis membranes described herein can enhance the rejection of specific compounds by such membranes. In particular, the rejection of sulfuric acid, sodium hydroxide, sodium nitrate and various organic compounds, such as isopropanol, can be affected by these treatments. Moreover, the rejection of common salts, such as sodium chloride, may also be enhanced by these treatments. Not all rejections of all compounds are necessarily affected to the same degree by various treatments. Sulfuric acid rejection can frequently be employed to indicate whether or not the treatment has in fact affected rejection of the membrane. Advantageously, the aqueous feed solution contains less than about 4 weight percent sulfuric acid, so as to avoid deleterious effects and excessive osmotic pressure. However, it is desirable to evaluate any membrane with the particular stream with which said membrane will be employed in order to determine the effectiveness of this treatment in enhancing rejection of specific solutes.

The following examples are presented to illustrate the invention, but are not otherwise intended to limit the subject invention. All parts and percentages are by weight unless otherwise indicated. Passage of a solute is in percent and is calculated by subtracting the rejection of said solute in percent from 100. Water flux is reported in gallons per square foot (of membrane) per day (gfd). The concentration of the solute in the feed water is specified, as is the pressure of the feed during evaluation of the membrane performance. The temperature of the feed water during these reverse osmosis tests is ambient, generally about 18 degree. to 25 degree. C., and flux data were then normalized to 25 degree. C. using standard tables available for commercial membranes of the type treated.

The membrane used in the examples is generally a composite crosslinked polyamide membrane having a polysulfone support and a desalinizing layer prepared by the interfacial polymerization of meta-phenylene diamine in an aqueous medium with trimesoyl chloride in an organic medium and is prepared in accordance with U.S. Pat. No. 4,277,344. This membrane is available from FilmTec Corporation under the designation FT30 membrane. If the membrane is dried, it is desirable to treat with a surface active agent prior to drying to make the membrane more readily wettable.

EXAMPLE 1

A commercially available FT30 membrane is evaluated in Comparative Experiment 1 employing a 3.2 percent aqueous sodium chloride solution at 200 psi, a sulfuric acid solution of pH 1 at 400 psi and a sodium hydroxide solution of pH 12 at 200 psi in three sequential reverse osmosis tests. A sample of the same membrane as that used in Comparative Experiment 1 is then treated with 1 percent peracetic in an aqueous solvent for 24 hours at about 25 degree. C. in Example 1. The treated membrane is then tested sequentially with sodium chloride, sulfuric acid, and sodium hydroxide feed streams like those used in Comparative Experiment 1 and the results are tabulated in Table I.

TABLE I
FC Tests 3.2% NaCl H.sub.2 SO.sub.4 (pH 1) NaOH (pH 12) at 200 psi at 400 psi at 200 psi Comparative Solute Solute Solute Experiment Example Treatment Flux Passage Flux Passage Flux Passage

Control	33	4.3	33	14	35	15	--	1	1%	Peracetic	27	1	1	20	1	25	4.9	acid	2	--	Lak
formed FT-30	14	0.8	24	7	21	4.8	control														

EXAMPLES 2-3

In Comparative Experiment 9 another sample of FT30 membrane is evaluated in reverse osmosis tests and the results of these tests are shown in Table II. A sample of membrane like that employed in Comparative Experiment 9 is then treated with 100 parts per million of sodium hypochlorite for 24 hours at about 25 degrees. The treated membrane is then evaluated in a series of reverse osmosis tests and results of these test are tabulated in Table II as Comparative Experiment 9.

RO

TABLE 11															NO				
Tests	0.2% NaCl	H.sub.2	S	sub.4	NaOH	at 200 psi	at 400 psi	at 210 psi	Comparative										
Sol.	Sol.	Sol.	Experiment	Example	Treatment	Flux	Passage	Flux	Passage	Flux	Passage	Flux	Passage	Flux	Passage				
Control	1	29	4	9	34	16	28	27	4	--	1% H.sub.2	O.sub.2	neutral pH	18	4.4	22	24		
5	--	1% H.sub.2	O.sub.2	28	5.6	13	17	27	29	4	--	1% H.sub.2	O.sub.2	21	9.2				
0	sub.2	+ 1% acetic	30	6	22	16	27	27	acid	7	--	1% H.sub.2	O.sub.2	+ 1% NaOH	22				
4	4	36	18	36	11	(pH 9)	--	2	1% peracetic acid	24	5	6.3	24.7	25	6.3	(pH 1.5	1		
hour)	--	3	1% peracetic acid	23	2.8	22	2	1	24	4.6	(24 hour)	8	--	Control	21	9.2	20		
18	24	21	9	--	100 ppm NaCl	14	hours	27	3.4	25	1.2	6.2	49						

From the data in Table II it is apparent that peracetic acid significantly increased the rejection of the membrane for all solutes evaluated with little impact on the flux of said membrane. The membrane samples treated with hydrogen peroxide at various pH's showed little decrease in sulfuric acid passage.

The membrane treated with sodium hypochlorite showed enhanced water flux and salt rejection as is taught in U.S. Pat. No. 4,277,844. The sulfuric acid rejection of the membrane was increased with minimal decrease in flux. However, the sodium hypochlorite treatment in combination with sodium hydroxide testing results in a membrane with a very high flux and a very high solute passage.

EXAMPLES 4-6

Two samples of a commercial FT30 membrane are tested to determine the water-flux and solute passage with four different feed streams in Comparative Experiment 10. The feed streams include 0.2 percent sodium chloride, 0.2 percent sodium nitrate, sulfuric acid at a pH of 1 and sodium hydroxide at a pH of 12. All tests, except the sulfuric acid, are conducted at 200 psi. The sulfuric acid test is conducted at 400 psi. Samples of membrane like those evaluated in Comparative Experiment 10 are treated with 0.1 percent aqueous peracetic acid in Example 4, with 0.1 percent periodic acid in Example 5 and with 1,000 parts per million chloramine in Example 6. All the treatment solutions are aqueous solutions and the treatments are for a period of three days at a temperature in the range of about 25 degree C.

The treated membranes were then evaluated in reverse osmosis tests and the results are tabulated in Table III.

TABLE III

															RO	
Tests 0.2% NaCl 0.2% NaNO ₃ H ₂ SO ₄ pH NaOH, pH 12 at 200 psi at 200 psi at 400 psi at 200 psi															Experiment	
Example Treatment															Flux Passage	
															10 --	
Control	17	12.3	21	16.1	21	13.5	18	17	16	8.2	20	7.2	23	13.9	17	16 -- 4 1.1%
Peracetic Acid	14	4.2	18	7.4	19	1.9	17	8	15	4.6	19	8.2	28	2.2	18	8 5 0.1% Periodic
Acid	33	5.4	34	10.1	43	2.9	53	23	33	5.1	24	10.8	42	2.9	53	23 6 1000 ppm Chloramine
	34	10.1	36	11.5	43	5.4	40	13	34	10.6	--	15.1	42	6.9	39	14

The peracetic acid treated membranes generally show the lowest solute passage with all of the solutes after treatment. The periodic acid treatment shows generally higher fluxes than the membrane prior to treatment and reduced solute passage for sulfuric acid and sodium chloride. The solute passage of sodium nitrate after the periodic acid treatment was lower than the FT30 control membrane but higher than the peracetic acid-treated membrane. The periodic acid treated membrane showed very high flux and poor solute passage in testing with sodium hydroxide. The chloramine-treated membrane also showed higher fluxes than the control, but the solute passages were generally comparable after chloramine treatment to that of the membrane prior to the treatment with the exception of the sulfuric acid solute passage which was reduced by more than 90 percent.

EXAMPLES 7-9

In Comparative Experiment 11 a FT30 membrane is evaluated in reverse osmosis tests with four solutions in a manner similar to Comparative Experiment 10. Two samples of the membrane are then treated with either peracetic acid, periodic acid, or chloramine in the general manner of Examples 4, 5 or 6, respectively, except that the treatment was 24 hours in duration. The results of the reverse osmosis tests of the control and treated membranes are tabulated in Table IV.

TABLE IV

															RO	
Tests 0.2% NaCl 0.2% NaNO ₃ 3 1000 ppm IPA H ₂ SO ₄ pH NaOH, pH 12 at 200 psi at 200 psi at 200 psi at 200 psi															Comp. Membrane	
Solute Solute Experiment Example Treatment															Flux Passage	
Passage Flux Passage Flux Passage															11 --	

Control 33 2.5 26 14.8 39 19 36 8.4 32 8.8 34 2.6 38 15.4 41 19 26 8.4 33 8.1 19
 0.1% 24 1 3 27 6.8 30 16 26 0.5 22 5.6 Peracetic Acid 24 1.2 26 5.1 28 16 25 1.7
 21 8.4 11 8 0.1% 21 2.6 23 10.9 28 22 23 5.2 19 7.4 Periodic Acid 22 4.1 25 14.7
 25 28 23 6 3 20 8 6 11 9 1000 ppm 24 1 7 26 5.5 26 27 15 1.6 26 8.4 Chloramine 24
 2.3 17 7.2 28 28 26 1.8 17 5.7

The water flux of all the membranes is somewhat reduced by the treatments but the solute passage is likewise reduced with the exception of the membranes treated with periodic acid and chloramine, which show increased solute passage for isopropyl alcohol.

EXAMPLES 10-13

A composite crosslinked polyamide membrane intended for use in seawater desalination and available commercially under the designation SW30HR from FilmTec Corporation is evaluated with simulated seawater containing 3.5 percent mixture of sodium chloride and other salts (on an anhydrous basis) at 800 psi. The SW30HR membrane is similar in composition to the FT30 membrane. The composition of the simulated seawater is as follows:

		Percent by Weight	
Na ₂ SO ₄ .sub.4	9.75	CaCl ₂ .sub.2	2.765
KCl	1.645	NaHCO ₃ .sub.3	0.477
KBr	0.238	H.sub.3	
BO ₃ .sub.3	0.071	SrCl ₂ .sub.2	0.095
NaF	0.017		

The flux and solute passage of two samples of this membrane are tabulated in Table V as Comparative Experiment 12.

Samples of the SW30HR control are then treated with 0.1 percent aqueous peracetic acid for 24 hours in Example 10. The flux and solute passage of the treated membrane with simulated seawater is tabulated in Table V.

The SW30HR membrane in two samples is treated with 0.1 percent periodic acid for 25 hours. The reverse osmosis test results for these samples are tabulated in Table V as Example 11.

TABLE V		RO Tests 3.5% SSW at 800 psi	
Comparative	Solute Example	Example Treatment	Flux Passage
		12 --	SW30HR Control 13 1.5 " 14 1.5 " 15
0.1% Peracetic Acid, 11	0.4	24 hrs. "	11 0.4 -- 11 0.1% Periodic acid, 15 1.4 25
hrs. "	15 1.6	-- 12 1000 ppm Chloramine	25 1.0 " 24 1.7 -- 13 1000 ppm
Chloramine 11	0.6	adjusted to pH 1 "	10 0.6

Two samples of the SW30HR membrane are treated with 1000 parts per million chloramine in water for 20 hours in Example 12. The reverse osmosis test results indicated a higher water flux and moderately higher solute passage.

In Example 13, the SW30HR membrane was also treated with 1000 parts per million chloramine but in a solution adjusted to a pH of 1. The water flux of this treated membrane was slightly lower than prior to treatment and the solute passage was marginally increased.

EXAMPLE 14

A commercially available FT30 membrane is coated with 85 percent phosphoric acid and treated at 120 degree. C. as generally described in U.S. Pat. No. 4,765,897. It is then incorporated into spiral wound reverse osmosis elements.

A clean sample of this membrane in spiral element form is treated with 0.1 percent peracetic acid for 16 hours. The resulting membrane element along with an untreated control, is then treated with a tannic acid colloid as described in U.S. Pat. No. 4,765,897. Both membranes were subjected to the following series of tests: (1) tested on 0.2 percent MgSO₄.sub.4 at 70 psi, (2) stored in a biostatic storage solution for 15 days, (3) retested on 0.2 percent MgSO₄.sub.4 at 70 psi, and (4) tested on 0.2 percent H.sub.2 SO₄.sub.4 at 70 psi. Results appear in Table VI.

TABLE VI

Percent MgSO₄.sub.4 0.2 percent MgSO₄.sub.4 0.2 percent H₂SO₄.sub.2 SO₄.sub.4 at 100-
 Retest* at 70 psi at 70 psi Flux Percent Flux Percent Flux Percent Treatment 100-
 Rejection (gpd) Rejection (gpd) Rejection

Comparative Control 330 98.8 281 98.1 296 25.8 Experiment 2: Example 1 of 100-
 peracetic 262 99.1 228 98.4 241 93.2 acid for 16 hours followed by tannic acid
 colloid

*After storage for 15 days in biostatic solution consisting of 1.0 percent by
 weight sodium metabisulfite dissolved in 80:20 water:propylene glycol.

CLAIMS:

What is claimed is:

1. A method of treating a composite crosslinked polyamide reverse osmosis membrane comprising: contacting a composite membrane having a crosslinked polyamide discriminating layer with a solution of an effective amount of a compatible oxidizing reagent, in quality and/or quantity sufficient for providing the membrane with properties for enabling the passage through the membrane of H₂SO₄.sub.2 in a 2 percent aqueous solution at 400 psig and 15.degree. to 25.degree. C. to be reduced by at least 30 percent relative to the membrane prior to treatment and the water flux of said membrane to be reduced by not more than 50 percent after treatment.
2. The method as described in claim 1 wherein the polyamide discriminating layer is derived from reactants comprising (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acyl halide groups.
3. The method as described in claim 2 wherein reactant (a) is a phenylenediamine.
4. The method as described in claim 2 wherein (b) is trimesoyl halide, cyclohexane-1,3,5-tricarboxyl halide, mixtures thereof or mixtures of either with isophthaloyl halide or terephthaloyl halide.
5. The method as described in claim 4 wherein (b) comprises at least 50 mole percent trimesoyl halide and (a) is at least 50 mole percent phenylenediamine.
6. The method as described in claim 5 wherein the polyamide discriminating layer is formed by interfacial polymerization of (a) and (b) on a microporous substrate.
7. The method as described in claim 6 wherein (a) comprises at least 50 mole percent m-phenylenediamine.
8. The method as described in claim 7 wherein the substrate is polysulfone.
9. The method as described in claim 8 wherein the membrane is contacted with an aqueous solution of chloramine.
10. The method as described in claim 8 wherein the membrane is contacted with periodic acid.
11. The method as described in claim 8 wherein the membrane is contacted with peracetic acid.
12. The method as described in claim 2 wherein the membrane is contacted with a peroxycarboxylic acid of less than 300 molecular weight, periodic acid, N-chloramine or N-bromamine.
13. The method as described in claim 12 wherein the membrane is contacted with peracetic acid.
14. A treated composite crosslinked polyamide membrane prepared by a process comprising contacting a crosslinked polyamide discriminating layer of a reverse

osmosis composite membrane with a solution of an effective amount of a compatible oxidizing reagent in quality and/or quantity sufficient for providing the membrane with properties for enabling the membrane after treatment to have a water flux of at least 50 percent of the membrane prior to treatment and to enable passage of H.sub.2 SO.sub.4 in a 2 percent aqueous solution at 400 psig and 25.degree. C. to be reduced by at least 30 percent relative to the membrane prior to treatment.

15. The membrane as described in claim 14 wherein the polyamide discriminating layer is derived from reactants comprising (a) a compound or polymer bearing at least two primary amine groups and (b) a compound or polymer bearing an average of more than two carboxylic acid halide groups.

16. The membrane as described in claim 15 wherein (b) is a trimesoyl halide, cyclohexane-1,3,5-tricarbonyl halide, mixtures thereof or mixtures of either with isophthaloyl halide or terephthaloyl halide.

17. The membrane as described in claim 15 wherein (b) comprises at least 5 mole percent trimesoyl halide.

18. The membrane as described in claim 17 wherein the polyamide discriminating layer is formed by interfacial polymerization of (a) and (b) on a microporous substrate.

19. The membrane as described in claim 18 wherein (a) comprises at least 50 mole percent m-phenylenediamine.

20. The membrane as described in claim 19 wherein (a) consists essentially of m-phenylenediamine, (b) consists essentially of trimesoyl chloride, the substrate is made from polysulfone and the membrane to be treated is clean.

21. The membrane as described in claim 20 wherein the compatible oxidizing reagent is peracetic acid.

22. The membrane as described in claim 15 wherein the compatible oxidizing reagent is a peroxycarboxylic acid with a molecular weight of less than 300, periodic acid, N-bromoamine or N-chloramine.

WEST**End of Result Set**

Generate Collection

LS: Entry 25 of 25

File: USPT

Apr 26, 1986

DOCUMENT-IDENTIFIER: US 3951920 A

TITLE: Permselective polymeric membrane prepared from polybenzimidazoles

BSPP:
Recently, permselective membranes comprising as a substrate a nitrogen-containing polymer including a wholly aromatic polyamide or polyhydrazide have been proposed (see, for instance, the specification of U.S. Pat. No. 3,567,632).

BSPP:
Typical examples of nitrogen-containing polymers disclosed in this U.S. Pat. are, poly(metaphenylene isophthalamide-terephthalamide) copolymers and poly(isophthalcyl hydrazide). Although in this reference it is disclosed that benzimidazole ring may be contained in an aromatic polyamide chain, it is not taught at all that nitrogen-containing linear polymers containing N-aryl-substituted-benzimidazole units as the main-chain-constituting units would be usable as substrate polymers for permselective polymeric membranes.

BSPP:
When a compound of the above formula (12-4) is reacted with a dicarboxylic dichloride at a molar ratio of 2:1, there is obtained an amideimine dicarboxylic acid expressed by the following formula ##EQU37## wherein Ar.sub.1, Ar.sub.2 and Q are as defined above, and B.sub.2 designates a dicarboxylic acid residue, or a derivative thereof, and when this amideimine dicarboxylic acid or its derivative is subjected to the cyclodehydration, an N-aryl-substituted benzimidazole is obtained. When such B.sub.2 and Q are as defined above, or its derivative is obtained. When such compound as expressed by the formula (12-5) or (12-6) or its reactive derivative is reacted with a diamine such as exemplified as in (b) above and, in the case of the compound of the formula (12-5), the cyclodehydration is subsequently effected, there is obtained a polybenzimidazole having the recurring units, each of which is composed of two recurring units of the above formula (14-4) that are alternating in the form reverse to each other, namely the recurring units expressed by the following formula ##EQU39## wherein Ar.sub.1, Ar.sub.2 and B.sub.2 are as defined above, and B.sub.3 is a diamine residue. In this method, preferably examples of the group Q are aryloxy and --NH.sub.2 groups. In case Q is --OH, it is also possible to convert it to the corresponding diacid chloride and then react it with a diamine. Further, in case Q is --OH, it is possible to obtain a polyamide-benzimidazole having the recurring units of the formula (14-5) by employing a diisocyanate such as exemplified in (d) above instead of the diamine.

BSPP:
When aromatic triamines and/or tetramines such as mentioned above are reacted with dicarboxylic halides in an interfacial solvent system comprising an inert organic solvent such as methylethylketone, cyclohexanone, tetrahydrofuran or tetramethylenesulfone and an aqueous alkali solution, or in low temperature solution polymerization system comprising a weakly basic solvent such as N-methylpyrrolidone, hexamethylphosphoramide or N,N-dimethylacetamide, corresponding polyamideimines are formed. When these polyamideimines are heated at a temperature exceeding 200.degree. C., preferably 250.degree. to 300.degree. C., for several hours in the solid state, or when they are heated in the solution state at 60.degree. to 200.degree. C. in the presence of an acidic substance such as cresol, acetic acid, formic acid, phosphoric acid, sulfuric acid, sulfonic acid, boric acid and hydrogen chloride, the cyclodehydration is caused to occur and there are obtained N-aryl-substituted benzimidazole polymers. As the

advantageous method for accomplishing the above reaction, there may be mentioned a method in which a polyamideimine if formed in a weakly basic aprotic polar solvent such as exemplified above and the as-obtained polyamideimine in the solution state is heated and cyclized by employing as a catalyst the hydrogen halide formed as a by-product in the above polyamideimine-forming reaction, thereby to convert the polyamideimine to the intended N-aryl-substituted benzimidazole polymer. In this advantageous method, the hydrogen halide remaining in the system may be converted to a lithium halide or calcium halide by addition of an oxide or hydroxide of lithium or calcium, and such metal halide may be used as a swelling agent in preparing a membrane from the N-aryl-substituted benzimidazole polymer, which feature will be detailed hereinafter. Further, at the cyclization step, in order to adjust the catalytic activity of the hydrogen halide, a lower alkylene oxide may be added to convert a part of the hydrogen halide to a haloalcohol.

BSFR:

In the dissolution of the substrate polymer, it is preferred that inorganic salts such as lithium chloride, lithium bromide, lithium nitrate, calcium chloride, calcium bromide, calcium nitrate and magnesium perchlorate, and organic compounds such as urea, ethyleneglycol, glycerine and formamide are added as low molecule compounds (c) being soluble in both the aprotic polar solvent (b) and a non-solvent (d) for the substrate polymer (a), which will be detailed hereinbelow, and having a molecular weight not exceeding 500. Inorganic salts such as exemplified above are especially preferably used as low molecule compounds (c). The dissolution of the low molecule compound (c) into the aprotic polar organic solvent (b) may be effected at any time. Namely, such low molecule compound (c) may be dissolved in the organic solvent (b) before, during or after the dissolution of the substrate polymer (a) into the solvent (b).

BSFR:

The permselective polymeric membrane of this invention can be clearly distinguished from the membrane of the above-mentioned U.S. Pat. No. 3,567,632 in that the substrate polymer of the permselective membrane of this invention contains N-aryl-substituted groups in its main chain, and by dint of the presence of said N-aryl-substituted groups, the permselective membrane of this invention has a permselectivity highly improved over the permselective membrane of said U.S. Pat. No. 3,567,632. As is seen from Examples given hereinbelow, when poly(metaphenylene isophthalamide/terephthalamide) copolymer which is a typical instance of the substrate polymer of said U.S. Patent is compared with the polyamide-benzimidazole of this invention, the polymer of this invention can be formed into a membrane more easily and the permeation characteristics, especially permselective permeability, of the membrane formed from the polymer of this invention are highly improved over those of the membrane formed from the polymer of said U.S. Patent.

DEIR:

In accordance with the method disclosed in the specification of U.S. Pat. No. 3,518,234, a polyamideimine having an inherent viscosity of 0.35 (measured at 30.degree.C. as a solution of 0.5 g polymer in 100 ml of N-methylpyrrolidone, values of the inherent viscosity given hereinbelow are those determined in this way unless otherwise indicated) was prepared from terephthaloyl chloride and 2,4-diaminodiphenylamine by the interfacial polycondensation employing the methylethylketone-water system. This polyamideimine was treated at 280.degree.C. for 3 hours in a nitrogen atmosphere to obtain a polyamidebenzimidazole having an inherent viscosity of 1.43. As a result of the infrared absorption spectrum analysis, it was found that the conversion to the polyamide-benzimidazole was more than 95%, and this polymer had the recurring units expressed by the following formula ##SPC1##

EEFF:

This polyamide-benzimidazole was dissolved in N-methylpyrrolidone so that the polymer concentration was 15% by weight, and lithium chloride was further dissolved therein in an amount of 20% by weight based on the polymer weight. The resulting solution was filtered with a microfilter and cast in a thickness of 60 μ m on a smooth glass plate at room temperature by means of a doctor knife. The casting was dried at 130.degree.C. for 15 minutes, and it was then dipped into methanol maintained at 30.degree.C. for about 20 minutes together with the glass plate. The film was peeled off from the glass plate and dipped in a great quantity of water at room temperature all night long.

DEPR: The Nr/s value of the polyamideimine (1) was calculated according to the disclosure of the above-quoted U.S. Pat. No. 3,567,632, and it was found that the value was 6.5 and the polyamideimine was included in the scope of said U.S. Patent. Similarly, the Nr/s value of the polyamide-benzimidazole (2) was calculated, and it was found that the value was 12 and the polymer (2) was outside the scope of said U.S. Patent.

DEIR:
III. A copolyamideimine was prepared from 75 mole % of terephthaloyl chloride, 25 mole % of fumaryl chloride and 2,4-diaminodiphenylamine by the interfacial polymerization method using a methylethylketone-water system, and the resulting polyamideimine was dissolved in N-methylpyrrolidone containing a small amount of hydrochloric acid, following which the solution was stirred at 120 degree C. for 2 hours to obtain an intended polymer. The structure of the polymer was determined by the infrared absorption spectrum analysis.

DETL.
Table 4

Content of Membrane	Example	Additive	membrane thickness	Water flux	Salt flux	No.
Kind	Amount** (%)	(.mu.)	(.mu.g/cm.sup.2 /sec)	(.mu.g/cm.sup.2 /sec)		
						7 --
						LiCl 2 24 3 5 16 0 0.013 10 LiCl

Content of Membrane		Example		Additive		Membrane		Permeability		Coefficient		Permeability		Coefficient						
Kind Amount** (%)		(mu.)		(mu.g/cm.sup.2 /sec)		(mu.g/cm.sup.2 /sec)		(mu.g/cm.sup.2 /sec)		(mu.g/cm.sup.2 /sec)		(mu.g/cm.sup.2 /sec)		(mu.g/cm.sup.2 /sec)						
18.4	13	5.8	0.005	8	LiCl	1	21.8	5	10.0	0.010	9	LiCl	2	24.3	5	10.0	0.013	10	LiCl	5
5.6	17	57.0	0.015	11	LiCl	10	54.5	13	150.0	0.130	12	LiCl	20	56.0	30	295.0	0.125			
13	CaCl.sub.2	1	22	0.4	7.4	0.085	14	CaCl.sub.2	3	31.0	14	12.4	0.053	15	CaCl.sub.2					
5	37.0	5	44.3	0.094	16	CaCl.sub.2	10	46.0	18	131.0	0.234	17	CaCl.sub.2	20	65.5	23				
3	10	0.253	18	Mg(ClO.sub.4).sub.2	20	21.2	21	8.3	0.003	19	urea	15	24	3	18	11.2				
0	0.51	20	glycerine	20	31.0	28	10.1	0.024	com-	LiCl	20	42	86	0.93	parison*					
generative polymer was used as																				

*Aromatic polyamide prepared in Example 1 as a comparative polymer was used as the substrate polymer. **The amount of the additive was expressed in terms of the percent by weight based on the polymer weight.

LETL:		Substrate Polymer		Copolyamide-		Water	
Table 6							
Polyamide benzimidazole (comparison)							
Content (%)	61	53	Membrane thickness (.mu.)	53	50	Water flux (l/m.sup.2 /hr)	32.8
17.6	Water permeability Wp		455	244	Salt rejection (%)		96.0 96.5

210/500.38

WEST☐ Generate Collection

L5: Entry 2 of 25

File: USPT

Dec 19, 2000

DOCUMENT-IDENTIFIER: US 6162358 A
TITLE: High flux reverse osmosis membrane

ABPL:
Reverse osmosis membranes with improved water flux and excellent solute rejection characteristics are formed by interfacial reaction of an essentially monomeric polyamine reactant having an average of at least two amine functional groups with an essentially monomeric amine-reactive reactant having an average of at least 2.05 acyl halide functional groups, the polymerization reaction being conducted in the presence of a monohydric phenol on the surface of a porous substrate. A specific example is a high flux composite membrane prepared by coating a porous substrate with an aqueous solution containing about 0.1-20 wt % m-phenylenediamine and 0.1-9.9 wt % phenol, and interfacially contacting the coated substrate with a nonaqueous solution of about 0.01-10 wt % trimesoyl chloride for a time sufficient to form a polyamide coating, followed optionally by one or more washing and drying steps to remove the nonaqueous solvent and most or all of residual unreacted chemicals.

BSFR:
The present invention relates to reverse osmosis membranes useful in water purification and aqueous separations, and more particularly to interfacially synthesized polyamide composite membranes having improved flux. The present invention also relates to processes for preparing the membranes.

BSPR:
It is known that semipermeable membranes useful in various separations can be made by interfacial polymerization processes conducted on the surfaces of porous substrates. In particular, a variety of semipermeable membranes known in the art as thin-film-composite membranes have been under development since the 1960s, resulting in commercial products now widely used in water purification, brackish water desalting, and potable water production from seawater. Principal among these membranes are aromatic polyamides prepared by interfacial reaction of aqueous aromatic polyamines with nonaqueous polyacyl halides, wherein the interfacial reaction is customarily performed on the surface of porous polysulfone substrates, the latter being usually further supported by a backing of a woven or nonwoven fibrous polyester or polyolefinic web. These are commonly referred to as thin film composite membranes in the art. Most of the current membranes of this type find their origin in methods and compounds originally taught in U.S. Pat. No. 4,277,344, issued to Cadotte, wherein aromatic diamines were interfacially reacted with aromatic polyacyl halides, trimesoyl chloride being the most preferred polyacyl halide. The commercial success of interfacially formed, aromatic polyamide membranes made according to the teachings of Cadotte has resulted in various versions thereafter with equivalent or improved performance. Particularly noteworthy in commerce are membranes with competitive performance characteristics made by the method disclosed in U.S. Pat. No. 4,872,984, wherein an amine salt is included in the aqueous aromatic polyamine solution employed in the interfacial reaction step.

BSFR:
An area of continuing interest and need is to provide reverse osmosis membranes having greatly improved flux while maintaining solute rejection characteristics. Advantages to be derived from development of such membranes include less expensive membrane process equipment and lower energy consumption due to lower fluid pressures and pumping requirements. Efforts toward this end have included variations in the amines and acyl halides used in the interfacial polymerization, and the usage of various processing and flux-inducing additives. For example,

11/28/01 7:24 PM

BSFR: This invention provides reverse osmosis membranes which have a surprisingly improved flux of water when contacted with a pressurized feed water, and yet retain highly effective rejection characteristics toward solutes such as inorganic salts dissolved in the pressurized feed water. These membranes are formed by the interfacial reaction of an essentially monomeric polyamine reactant typically having an average of about two amine functional groups per monomer unit, with an essentially monomeric amine-reactive reactant preferably having an average of at least about 2.05 acyl halide functional groups per monomer unit, this interfacial reaction being conducted in the presence of a monohydric phenol, a polyamidic reaction product being formed thereby. The polyamidic reaction product resulting from the interfacial reaction is deposited on and/or within the surface of a porous substrate as a semipermeable thin coating. The action of the monohydric phenol in modifying the interfacially formed polyamidic reaction product provides semipermeable coatings having unexpectedly enhanced water flux while retaining excellent semipermeable characteristics. The monohydric phenol is believed to be incorporated into the polyamidic reaction product in minor amounts, thereby modifying this reaction product chemically through the presence of pendant phenolate ester groups.

ESPR.

In an embodiment of the invention, the semipermeable membranes of the present invention may be prepared by coating a porous substrate with an aqueous solution of an aromatic polyamine containing the monohydric phenol as an additive in this aqueous solution, then exposing the coated porous substrate to a nonaqueous polyacyl halide solution. The porous substrate may consist of an inorganic material such as a porous ceramic or glass. Preferably, however, the porous

substrate will consist of a polymeric material. An optimal substrate material preferably contains inter-connected pores in its matrix that are of sufficient size to permit essentially unimpeded passage of permeate through the substrate, while having surface pores of sufficiently small size to structurally support the thin interfacial layer deposited thereon, such that the thin interfacial layer can withstand contact with a pressurized feed solution at from 50 to as high as 1,500 psig without any undue damage to its integrity. The surface pores of the porous substrate preferably range in size from about 1 millimicron to about 100 millimicrons at the surface supporting the deposited interfacial layer. The pores of the porous substrate may vary considerably beneath this surface layer, and may range from 1 millimicron to as high as 25 microns. A graded porosity changing from a finely porous support surface to a coarsely porous back surface is particularly preferred.

BSIR:

Examples of polymeric porous substrates which may be used to prepare the desired composite membranes of the present invention include porous substrates made from polymer resins such as polysulfone, polycarbonate, polyphenylene oxide, polyimide, polyetherimide, polyetheretherketone (PEEK), and other such engineering plastics. Various polyolefins and halogenated polyolefins such as polypropylene, polymethylpentene, polyvinyl chloride and polyvinylidene fluoride may also be employed. Methods of making porous films and fibers from these various polymers are known in the art, particularly in reference to the preparation of ultrafiltration and microfiltration membranes. The porous substrate is preferably of a composition that is not adversely affected in the preparation of the composite membranes, such as by chemical attack by the solutions used in the interfacial reaction or by processing or drying steps in the making of the membranes of the invention. Porous substrates made of polysulfone resins are particularly known and used in the art.

ESPR:

The finely porous surface of the porous substrate is impregnated with a solution of one of the two interfacial reactants. Wherein one of the two solutions is aqueous in nature, it is almost always preferable to impregnate the porous substrate with the aqueous solution. This solution customarily will contain a polyamine reactant, this polyamine reactant being capable of reacting with polyacyl halides to form polyamides. Impregnation of the substrate with the solution of the interfacial reactant need not be limited to the finely porous surface alone, but may involve the back side of the porous substrate as well, including even a fibrous web support if present. It is generally not advantageous to intentionally impregnate the substrate backside and fibrous web, particularly if residual unreacted chemicals are to be removed by subsequent washing processes.

BSPR:

The polyamine reactant present in the amine solution preferably has a minimum of two amino groups per monomer, and more preferably consists of a monomeric aromatic chemical compound having at least two acyl-halide-reactive amino groups therein. Examples of polyamines useful in the invention include o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 1,3,5-benzenetriamine, 4-chloro-1,3-phenylenediamine, fluoro-analogs of 5-chloro-1,3-phenylenediamine, 3-chloro-1,4-phenylenediamine, and fluoro-substituted these chloro-diamines, benzidine, diaminobenzidines, alkyl and chloro-substituted derivatives of benzidine, and naphthylenediamines. Combinations of these amines may be employed as well. Oligomeric and polymeric polyamines may also be employed, but are generally not advantageous to use in place of the essentially monomeric polyamines as generally represented in the above list of examples. Preferred diamines include members of the group consisting of m-phenylenediamine, p-phenylenediamine, 1,3,5-benzenetriamine, 4-chloro-1,3-phenylenediamine, 5-chloro-1,3-phenylenediamine, 3-chloro-1,4-phenylenediamine, and fluoro-analogs of these chloro-diamines. Meta-phenylenediamine has been found to be particularly preferred as a polyamine reactant in the interfacial formation of the membranes of the invention.

BSPR:

The monohydric phenol present in the aqueous solution of the polyamine reactant as an additive may consist of any chemical compound having in its chemical structure a single hydroxyl group attached to an aromatic ring. Such compounds may contain either one ring or a plurality of rings in their chemical structure.

and may have substituent groups other than hydroxyl also attached to the aromatic ring or rings, but have one and only one hydroxyl group attached via an aromatic ring. Such compounds should show a minimum solubility of about 1.0 gram per liter in water within the temperature range of from about 1 degree C. to about 40 degree C. Such monohydric phenols preferably do not have substituent groups that spontaneously react ionically or covalently with aromatic amines in the aqueous polyamine solution such as to generate insoluble byproducts unsuitable to the intended interfacial reaction with the polyacyl halide reactant, or inactivate the polyamine reactant such that no useful interfacial membrane can be established on the porous substrate. Particularly preferred are simple one-ring phenolic compounds, including phenol, guaiacol, m-methoxyphenol, p-methoxyphenol, o-fluorophenol, m-fluorophenol, p-fluorophenol, o-cresol, m-cresol, and p-cresol. Guaiacol has shown particularly remarkable enhancement of membrane fluxes combined with retention of excellent salt rejections. These phenolic compounds may be used alone or in combination as flux-increasing additives in the polyamine reactant solution. The concentration of the monohydric phenol may vary in the range of from about 0.1 to about 9.9 wt % of the amine solution, more preferably from about 0.3 to about 5 wt %, most preferably from about 0.5 to about 1 wt %. Various substituted phenols will generally be limited to a range of less than 5 wt % due to natural solubility limits, and such limits can be determined easily through published solubility data, or in absence thereof, through simple solubility tests. Solubility of the monohydric phenol in an aqueous solution of a polyamine reactant may be further decreased at times by inclusion of other solutes, such as for example the amine salts described in U.S. Pat. Nos. 4,872,984 and 4,948,507. On the other hand, solubility limits of the monohydric phenols may be increased by addition of solubilizing agents to the polyamine reactant solution. Typical solubilizing agents include water-miscible solvents such as, for example, acetonitrile, acetone, or a low molecular weight alcohol. Particularly preferred is an alcohol such as isopropanol. Thus, in some embodiments of the invention, the solution of the polyamine reactant may include, in addition to the monohydric phenol one or more of the following: an amine salt, a surfactant, an acid acceptor, and a solubilizing agent such as isopropanol.

BSPE:

The monohydric phenols may associate with aromatic polyamines in solution by an acid-base pairing attraction, forming weak acid/weak base complexes. These complexes, if present, do not appear to interfere in the formation of the interfacial membranes of the invention.

BSPE:

Aqueous solutions of the polyamine and the phenolic compound additive preferably have a pH of less than 10, so that the phenolic compound is not converted to a phenolate salt. Amino groups are generally known to react with acyl halides at a far greater rate than phenolic hydroxyl groups. Conversion of the phenolic compound to the phenolate salt at high pH tends to greatly increase the chemical reactivity of the phenolic compound toward the acyl halide, resulting in an interfacial polymerization reaction product that may not necessarily be predominantly polyamidic, and may be subject to loss of optimal flux and salt rejection characteristics. Incidental incorporation of the phenolic compound into the desired polyamidic layer via ester linkages may occur, and is believed to result in a plurality of pendant phenolate ester groups within the polyamidic layer, and such pendant groups may contribute to structural disorder and enhanced hydraulic permeability in this substantially polyamidic reaction product.

BSPE:

Application of the aqueous solution containing the polyamine reactant and the monohydric phenol onto a porous substrate may be made by one of several methods including dipping, spraying, slot-die-coating, knife-coating, transfer roll application or sponging. Contact of the liquid solution with the porous substrate is generally maintained for a period of between 0.1 second and 10 minutes, preferably for a period of between 1 and 100 seconds, during which the finely porous surface of the porous substrate (the surface upon which it is desired to deposit the interfacial reaction product) becomes impregnated with the polyamine solution. Excess polyamine solution is then preferably removed by one or more methods, including for example draining, air-knife treatment, nip roller contact, squeeze roller contact, wire-wound rod contact, or sponging. Methods which do not physically mar the surface of the porous substrate are particularly preferred. It is found advantageous that remaining liquid solution on the top

surface of the porous substrate be further dried after removal of excess solution, generally by some type of air-drying method at ambient or mildly elevated temperatures within the range of about 15 to about 50 degrees C.

BSPE:

The top surface of the porous substrate coated with the polyamine reactant and monohydric phenol is then brought into contact with a nonaqueous solution containing the polyacyl halide reactant for a time sufficient to form a coherent film by interfacial reaction, i.e., chemical reaction at or approximate to the interface between the coated substrate and the nonaqueous solution. Such time may be for a period of between 0.1 second and 10 minutes, preferably of between 1 and 100 seconds. Application of the nonaqueous solution of the amine-reactive reactant may be by one of several methods including dipping, spraying, slot-die coating, knife-coating, transfer roll application or spreading. Application methods which do not cause any significant stirring at the solution interface are preferable, the dipping method being particularly preferred.

BSIF:

The polyacyl halide reactant consists of a chemical compound or combination of chemical compounds having a plurality of acyl halide groups ranging from a minimum of 2 to as high as 6 such groups per compound or combination. The polyacyl halide compounds may be aliphatic, cycloaliphatic or aromatic in nature, including isophthaloyl chloride, terephthaloyl chloride, 1,2,5-benzenetricarbonyl chloride (trimesoyl chloride), 1,2,4-benzenetricarbonyl chloride (trimellitoyl chloride), 1,2,3,4-furantetracarboxyl chloride, 1,2,5-cyclohexanetricarbonyl chloride, 5-isocyanato-1,3-benzenedicarbonyl chloride, and halo analogs of these compounds such as the carbonyl fluorides and carbonyl bromides. Polymeric polyacyl halides may also be employed, but are generally not advantageous to use in place of the essentially monomeric polyacyl halides as generally represented in the above list of examples. Aromatic polyacyl halides are preferred in making membranes according to this invention. Particularly preferred are trimesoyl chloride or combinations of trimesoyl chloride with isophthaloyl or terephthaloyl chloride.

BSFH:

For good interfacial film formation, it is highly preferable to develop crosslinking in the interfacial polymer formation step, and this is most conveniently done by having an average acyl halide functionality of at least about 2.05 groups per polyacyl halide reactant. Thus, a ratio of acyl halide functionality greater than 2, that is, 2.05 or higher, is customarily employed, and the resulting polyamide reaction product is accordingly crosslinked. In the case of a difunctional acyl halide such as isophthaloyl chloride, a minimal concentration of a higher functionality acyl halide such as trimesoyl chloride is desired so as to achieve a crosslinking composition having about 2.05 or greater average of reactive functional groups present. Trimesoyl chloride itself, having a functionality of 3, may be used alone to very good effect in the interfacial polymerization step with the polyamine reactant in producing a crosslinked polyamidic layer. The concentration of the polyacyl halide component in the nonaqueous solution may vary in a range from about 1.01 to about 20 wt %, more preferably from about 0.03 to about 5.0 wt %, most preferably from about 0.05 to about 1.0 wt %.

BSIF:

Nonaqueous solvents useful for polyacyl halide solutions include hydrocarbons, chlorinated hydrocarbons, and fluorochlorohydrocarbons. Nonaqueous solvents should be chosen such that no prominent solubility exists in water that would deleteriously affect the interfacial reaction, and further that no significant damage occur to the porous substrate to which the nonaqueous solvent may come into incidental contact. Particularly preferred from an environmental viewpoint are hydrocarbon solvents that are aliphatic and nonhalogenated, examples being hexane, heptane, octane, and various nonaromatic petroleum distillates. Such hydrocarbons may not necessarily hold some aromatic polyacyl halides in solution throughout the full concentration range that is preferred, but nevertheless will generally provide workable concentrations sufficient to the interfacial formation of coherent semipermeable films. Particularly preferred on the basis of safety as well as environmental factors are high flash point nonaromatic petroleum distillates.

BSPF:

Composite membranes formed by interfacial reaction between the polyamine reactant and the polyacyl halide reactant in the presence of the monohydric phenol may be further processed in steps conventionally known in the art, including washing, treatment with rewetting agents, and drying. Such steps may include passage of the freshly formed composite membrane through aqueous alkaline solutions for neutralization of acyl halide residuals, cold or hot water for extraction of unreacted chemicals, and dip or spray contact with rewetting agents such as glycerine, surfactants, or a combination thereof. Impregnation of washed membrane with rewetting agents is particularly desirable for membrane flux retention when such washed membrane is subjected to an oven drying step.

DEFF:

In the following examples, membranes were formed by interfacial polymerization on a porous polysulfone substrate coated on a nonwoven polyester fabric. The porous polysulfone substrate was prepared by applying a casting dope to a nonwoven polyester web in a continuous manner on a machine. The casting dope consisted of 15% by weight polysulfone resin dissolved in 70% by weight N,N-dimethylformamide and 15% by weight methyl cellosolve. The coated web was quenched in water to gel the polysulfone into a porous form, and residual solvent was removed by rinsing in water. Sections of the resulting porous polysulfone substrate were cut into 8-inch by 12-inch pieces and used in hand fabrication of membrane samples according to the invention.

DEFF:

Each sample of porous polysulfone substrate was first contacted with an aqueous solution of a reactive polyamine and monohydric phenol additive, followed by air-drying of the coated surface, then contacted with a nonaqueous solution of an acyl halide, followed by oven drying to remove the nonaqueous solvent. The resulting membrane was neutralized in a bath containing 0.2 wt % sodium carbonate and 2.3 wt % sodium sulfate for 20 seconds, then rinsed in water for 12 minutes. Any significant defects in the hand-coated membrane were made visible by spraying the membrane with a dye solution containing 500 mg/liter of rhodamine B, which preferentially stained polysulfone in any regions where the interfacial membrane incompletely covered the polysulfone substrate. The membranes were then dipped in an aqueous solution containing 0.3 wt % sodium lauryl sulfate and 5 wt % glycerine for 100 seconds, then dried in a 90.degree. C. oven for six minutes.

DEFF:

In addition to these examples, membranes were made with 3% phenol in the amine solution at MED concentrations of 2.0 and 4.0%, containing also 10% IPA to maintain clear solutions. At this particular concentration level of phenol, resulting membranes did not have complete surface coverage by the interfacial membrane, as indicated by dyeing, and no useful reverse osmosis test data were generated.

CICF:

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CCIF:

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CIFS:

210/500.38

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Generate Collection

L10. Entry 3 of 16

File: USPT

Dec 21, 1999

DOCUMENT-IDENTIFIER: US 5271843 A
TITLE: Chlorine-tolerant, thin-film composite membrane

BSPR:
This invention is generally concerned with the purification of liquids. Of particular interest is the treatment of water which contains unacceptable amounts of dissolved salts, such as seawater, brackish water or hard water. Such waters may be purified by forcing the water through a semipermeable reverse osmosis membrane, leaving behind the contaminants or salts which do not pass through the membrane.

BSPR:
A reverse osmosis membrane must reject a high fraction of the dissolved salts. It is also important that such membranes pass a relatively large amount of water (i.e., have a high water flux) through the membrane at relatively low pressures. In addition, the membrane must be tolerant to chlorine, which is often added as a disinfectant, since removal of the chlorine to protect the membrane may not always be effective.

BSPR:
In U.S. Pat. No. 3,904,519, McKinney et al. disclose the use of linear polyamides which are cast on a support and then crosslinked to form a reverse osmosis membrane. The polyamides are prepared by condensation of diamines with dicarboxylic acid chlorides and crosslinked by formaldehyde, irradiation, or diamines.

BSPR:
The formation of prepolymers for later reaction to make reverse osmosis membranes is discussed in the Final Report, OWRT Contract 14-34-001-6521 (March 1978) pages 7-10 and also U.S. Pat. No. 4,259,183. An improvement in salt rejection was sought by reacting piperazine (a cyclic aliphatic secondary diamine) with trimesoyl chloride, cyanuric chloride, and phosphorous oxychloride to produce a compound having amino groups which could be interfacially reacted with an acyl halide to form a reverse osmosis membrane. While improved salt rejection was obtained, the water flux was considered to be low. The same report suggested that monoamines might be used, particularly morpholine and diethanol amine, but stated that tests indicated that no beneficial effect was obtained.

BSPR:
The present inventors have now discovered a new method for preparing a reverse osmosis membrane and employing a new aromatic polyamine for interfacial reaction with an acyl halide or other amine-reactive group. The resulting membrane provides a high salt rejection with good water flux and good chlorine tolerance.

BSPR:
Semipermeable composite membranes useful for reverse osmosis as in desalinization of water are prepared by interfacial reaction of a polyfunctional amine-reactive compound, such as a polyacyl halide, with a preformed aromatic polyamine containing at least three and, preferably, four aromatic nuclei. The polyamine preferably is derived from an aromatic polyacyl halide, but other polyhalides may be substituted, such as cyanuric chloride, phosphorous oxychloride, phosphonyl chlorides, thionyl chloride, and sulfuryl chloride.

BSPR:
An advantage of the present invention lies - 20 in the use of an adduct as the basic unit for an interfacially formed semipermeable membrane. This adduct is

believed to minimize the formation of reaction products which have lower molecular weight and to promote the formation of more uniformly cross-linked membranes. When each reacting compound has a single multi-functional aromatic ring many products are possible. The thin film composite membrane formed may well be less uniform than would be desirable. The present invention reduces these problems since a higher molecular weight adduct is used to prepare the membrane. The adduct is soluble in solvents that are compatible with the porous support and can be interfacially reacted to form a uniform semipermeable membrane which provides good salt rejection, high flux, and chlorine tolerance when used in desalination of water.

BSIF:

The preferred starting materials for the adduct are the polyacyl halides. Examples of aromatic polycarboxylic acid halides which may be employed will include di- or tricarboxylic acid halides such as trimesoyl chloride (1,3,5-benzene tricarboxylic acid chloride), trimellitoyl chloride (1,2,4-benzene tricarboxylic acid chloride), isophthaloyl chloride, terephthaloyl chloride, trimesoyl bromide (1,3,5-benzene tricarboxylic acid bromide), trimellitoyl bromide (1,2,4-benzene tricarboxylic acid bromide), isophthaloyl bromide, terephthaloyl bromide, trimesoyl iodide (1,3,5-benzene tricarboxylic acid iodide), trimellitoyl iodide (1,2,4-benzene tricarboxylic acid iodide), isophthaloyl iodide, terephthaloyl iodide, as well as mixtures of di-tri-tricarboxylic acid halides, that is, trimesoyl halide and the isomeric phthaloyl halides. The di- or tricarboxylic acid halides may be substituted to render them more resistant to further environmental attack. Particularly preferred are aromatic acid halides selected from the group consisting of isophthaloyl chloride, trimesoyl chloride, trimellitoyl chloride, and terephthaloyl chloride.

BSPR:

If the substituent group is a halogen, it may be converted to an amino group by amination with alkali salts of amines, such as potassium amide with liquid ammonia as solvent. A disadvantage of displacement reactions of this type is that the amino entering group may not always occupy the same position on the aromatic ring vacated by the halogen.

BSPE:

The method just described involves a two-step process and has the advantage of providing essentially a single species of aromatic polyamine since the monoamine reactant cannot react twice with the polyfunctional acylhalide or crosslink to form polymers. However, the process does require more expensive and complex processing to produce the desired adduct. A second method of producing the polyamine involves the use of a single reaction, although separation is desirable to obtain the same adduct as the first method. A large excess (2 to 5) times stoichiometric) of a diamine is reacted with a polyacyl halide as illustrated in the following example using m-phenylene diamine and trimesoyl chloride. ##STR4## Since m-phenylene diamine is difunctional, the desired adduct shown is not the only possible product. In fact, the reactants have been used commercially to prepare semipermeable membranes by interfacial polymerization. However, for the present invention such polymerization is not wanted at this point and a large excess of m-phenylene diamine would be used to favor the formation of the polyamine. Purification by filtration, extraction, and washing would be used to arrive at the desired polyamine.

BSPE:

The membranes may be prepared by the method generally described by Scola et al. An aqueous solution of the polyamine is coated on a porous support material and the excess removed by drawing, rolling, sponging, air knitting or other suitable techniques. Thereafter, the surface of the coated support material is dried to the touch and then is contacted with an organic solution of a polyacyl halide. Since the porous support material surface is dry, the polymerized reaction product is formed within and/or on the porous support. The resulting composite is then cured to provide a semipermeable membrane which exhibits good water flux and good salt rejection as well as tolerance to chlorine.

BSPE:

The porous support material comprises a polymeric material containing pores which are of sufficient size to permit the passage of permeate through the support. In the preferred embodiment of the invention, the pore size of the porous support material will range from about 1 to about 5,000 nanometers. Examples of porous

support materials which may be used to prepare the desired membrane composite. The present invention may include such polymers as polysulfone, polycarbonate, microporous polypropylene, the various polyamides, polyamines, polyphenylene ether, and various halogenated polymers such as polyvinylidene fluoride.

BSPR:

The composite high flux membrane may be subjected to one or more optional post treatments. The membrane may be washed with an aqueous solution having a pH in the range of from about 9 to about 11. The solution may include a basic compound such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, and the like. The wash temperature may be in the range of from about 20 degree to about 100 degree C. for a period of time in the range of from about 1 to about 15 minutes. A post-treatment with acids, as described by Chau in U.S. Pat. No. 4,983,291, may also be used.

BSPE:

In the following examples the porous support was a polysulfone cast on a fabric backing. A trinitro adduct was prepared by reacting 3-nitroaniline with trimesoyl chloride and then the nitro groups were reduced to amino groups, thus producing the polyamine of the invention. Alternatively, the polyamine was formed by reacting an excess of m-phenylene diamine with trimesoyl chloride and then separating the desired polyamine from other products. The polyamine was coated onto the support, followed by contact with a polyacyl halide in an interfacial reaction to form semipermeable membranes. The membranes were tested in flat cells using 1"2" (25.4 mm.times.76.2 mm) samples of the membranes. A solution of 2 g/L of NaCl in water at a pH of 7-8 was used with a 220 psig (1520 kPa gauge) pressure applied to the membrane (equivalent to about 200 psi (2380 kPa) net pressure differential after accounting for the osmotic pressure). The water flux and salt rejection were measured and reported in the examples.

BSID:Interfacial Polymerization**DEPR:**

The trinitro adduct was reduced to a polyamine by reaction with a mixture of sodium formate and potassium hydrogen phosphate in NMP, following the procedure of Bakler and Sarussi. 210 g of the adduct and 2.2 L of N-methyl pyrrolidone (NMP) were placed in a flask equipped with a stirrer and condenser. Once the trinitro adduct was dissolved, 224 g of sodium formate and 243 g of potassium hydrogen phosphate were added to the flask and the mixture was heated to 20 degree C., the reflux temperature of the NMP. The reflux conditions were maintained for about 16 hours in a nitrogen atmosphere. Then, the mixture was cooled to room temperature and filtered to remove some of the salts.

DEPR:

The porous polysulfone support was immersed in an aqueous solution at pH 9 of 4.4% by weight of the polyamine of Example 1 and 15.5% by weight NMP for 12 seconds. Excess solution was removed by blowing with pressurized air from a hose and draining for a period of 6 minutes. The support coated with polyamine was then contacted with a 0.1% trimesoyl chloride (TMC) solution in naphtha for 15 seconds to form a membrane by interfacial polymerization. After 15 minutes at ambient temperature, the membrane was placed in a test cell and after one hour of testing with 0.2 wt.% NaCl water at 220 psig (1520 kPa gauge) a water flux of 12.1 gfd (gfd=gal/ft.sup.2-day) (900 l/m.sup.2-d) and a salt rejection of 98% were measured.

IEPR:

Example 2 was repeated except the drain time was shortened to 5 minutes. The resulting membrane had a water flux of 17.8 gfd (725 l/m.sup.2-d) and a salt rejection of 98.7%.

IEPR:

Example 2 was repeated except that the 0.1% TMC solution was replaced with 0.2% by weight isophthaloyl chloride (IPC). Membrane had a water flux of 8.9 gfd (360 l/m.sup.2-d) and 47.2% salt rejection.

DEPR:

Example 4 was repeated except that the polyamine solution was replaced with an

aqueous solution of 2% by weight m-phenylene diamine (MPDA), 1% by weight NMF, and 0.01% by weight sodium carbonate and 0.3% by weight IPC was used rather than 0.2% IPC. As expected, the membrane salt rejection of 9.3% was much lower than the 47.2% obtained in Example 4.

DEPR:
Example 2 was repeated except that the polyamine solution was adjusted to pH 1. The average performance of two samples was 18.7 gfd (762 l/m.sup.2 d) with a salt rejection of 97.5%.

DEPR:
Example 2 was repeated except that the polyamine solution was adjusted to pH 7. The average performance of two samples was 16.9 gfd (689 l/m.sup.2 d) with a salt rejection of 98.2%.

DEPR:
Example 2 was repeated except that the polyamine concentration was 5.5 wt.% and the NMF concentration was 19%. After four hours of testing, the membrane had a water flux of 11.4 gfd (464 l/m.sup.2 d) and a salt rejection of 99.3%.

DEPR:
A polyamine was prepared by reacting 14.7 g (136 mmol) of m-phenylene diamine with 2.0 g (7.5 mmol) of trimesoyl chloride in, as a solvent, 400 mL of dichloroethane. The product mixture was filtered off and dissolved in water to give a 0.2 wt. % solution. After filtering again, the solution was used to prepare semipermeable membranes by interfacial polymerization with a 0.1 wt. % trimesoyl chloride in naphtha in a manner similar to that used in previous examples. The resulting membrane was tested and found to have an average flux (2 samples) of 4.5 gfd (183.4 l/m.sup.2 d) and 98.9% salt rejection.

DEPR:
Example 2 was repeated except that the polyamine concentration was 5.0 wt. %, the NMF concentration was 15.4 wt. %, and the pH was reduced to 9.0 by adding HCl. The polyamine was interfacially reacted on the support by contact for 12 seconds with a 0.25 wt. % solution of trimesoyl chloride in naphtha. The resulting supported membrane was tested and the average (2 samples) flux was 19.5 gfd (794.6 l/m.sup.2 d) and the salt rejection 99.1%.

DEPR:
Example 11 was repeated except that a 2.0 wt. % solution of m-phenylene diamine in water with 100 ppm sodium carbonate replaced the adduct solution. The resulting membrane was tested and the average flux was 17.8 gfd (725.3 l/m.sup.2 d) and the salt rejection 99.3%.

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File: USPT

Apr 25, 1978

L11: Entry 1 of 3

US-PAT-NO: 4086215

DOCUMENT-IDENTIFIER: US 4086215 A

TITLE: Crosslinked organic polyamide or polyhydrazine permselective polymeric membranes

DATE-ISSUED: April 25, 1978

INVENTOR-INFORMATION:

NAME

Kurihara; Masaru

Tokizane; Seichi

Tanaka; Tatsundo

Tanimura; Masamitsu

Shimokawa; Yoichi

CITY

Otsu

Otsu

Otsu

Otsu

Otsu

STATE

ZIP CODE

COUNTRY

JA

JA

JA

JA

JA

US-CL-CURRENT: 525/419; 210/654, 525/420, 528/310, 528/328, 528/331, 528/332,
528/337, 528/341, 528/350, 528/352, 528/363

Full	Title	Citation	Front	Review	Classification	Date	Reference	Claims	KWIC	Draw Desc	Image
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2. Document ID: US 3993625 A

File: USPT

Nov 23, 1976

L11: Entry 2 of 3

US-PAT-NO: 3993625

DOCUMENT-IDENTIFIER: US 3993625 A

TITLE: Permselective polymeric membranes of organic polyamide or polyhydrazide

DATE-ISSUED: November 23, 1976

INVENTOR-INFORMATION:

NAME

Kurihara; Masaru

Ikeda; Kojiro

Hokoshi; Noriaki

Kobayashi; Akio

CITY

Otsu

Otsu

Otsu

Otsu

Kusatsu

STATE

ZIP CODE

COUNTRY

JA

JA




JA

JA

US-CL-CURRENT: 521/63; 210/500.33, 210/500.41, 521/64, 524/233, 524/909, 525/420,
528/172, 528/208, 528/210, 528/211, 528/337, 528/363, 528/367, 528/391

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